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Assessment of Electroless Plating for In-situ Repair of Monel Clad Q1N Steel Hull Valves in VICTORIA Class Submarines

Pierre R. Roberge
Robert D. Klassen

Department of Chem./Chem. Eng.
Royal Military College of Canada
PO Box 17000 Stn Forces
Kingston, ON
K7K 7B4

Contract Scientific Authority: Dr. Yueping Wang, (902) 427-0550 ext. 3035

Defence R&D Canada – Atlantic

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PO Box 17000 Stn Forces
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Canada K7K 7B4

Contract Scientific Authority: Dr. Yueping Wang (902) 427-0550 ext. 3035

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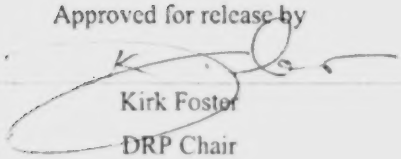
Approved by

R. Morchat

H/EMat

Approved for release by



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Abstract

This project was an exploration of the feasibility of repairing Monel-clad Q1N steel valves, in-situ, using electroless nickel (EN) plating. In this technique, a layer of EN is deposited chemically on the damaged surface. The resistance of the EN coating to both uniform and localized corrosion was compared with that of Monel using electrochemical techniques (i.e. electrochemical impedance spectroscopy and cyclic polarization), and passive crevice corrosion test.
A cleaning technique was developed to allow EN to coat over the bottom of corrosion pits on Monel. The uniform corrosion rate of an EN coating in artificial seawater was measured by electrochemical impedance spectroscopy and found to be less than that of Monel. The tendency towards pitting and crevice corrosion of an EN coating was also found to be better than that of Monel. The main conclusion from this work is that an EN coating would be a viable solution to repair Monel-clad submarine valves.
Recommendations were also made to further develop the EN technique to repair Monel-clad Q1N steel valves in situ.

Résumé

Les travaux du présent projet visaient à étudier la faisabilité d'effectuer des réparations in situ de vannes de coque en acier Q1N revêtues de Monel, par dépôt autocatalytique (DA) de nickel. La technique consiste à effectuer le dépôt chimique d'une couche de nickel par DA sur la surface endommagée. On a comparé la résistance à la corrosion uniforme et à la corrosion locale (par piqûres) du revêtement de nickel obtenu par DA et celle du revêtement de Monel, à l'aide de techniques électrochimiques (soit la spectroscopie d'impédance électrochimique et la polarisation cyclique) et d'essais de corrosion fissurante passive.
On a mis au point une technique de nettoyage permettant d'effectuer le DA de nickel au fond de piqûres de corrosion présentes à la surface du revêtement de Monel. On a mesuré la vitesse de corrosion uniforme d'un revêtement de nickel par DA dans l'eau de mer artificielle, à l'aide de la spectroscopie d'impédance électrochimique; les résultats indiquent que la vitesse de corrosion du revêtement étudié est inférieure à celle du Monel. De plus, le revêtement de nickel par DA résiste mieux que le Monel à la corrosion locale (par piqûres) et à la corrosion fissurante. Les principaux résultats de nos travaux indiquent que le revêtement de nickel par DA constitue une solution de remplacement éprouvée, lorsqu'il faut réparer des vannes de coque de sous-marins revêtues de Monel. Le rapport contient aussi des recommandations portant sur l'exécution de travaux additionnels visant à améliorer la technique de DA de nickel afin de pouvoir effectuer la réparation in situ de vannes de coque en acier Q1N revêtues de Monel.

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Executive Summary

Introduction
Recent inspection of the hull valves in HMCS VICTORIA revealed damage on the Monel-clad Q1N steel valves, most seriously in the form of grooves or pits. Although most damage can be removed by slightly grinding the cladding material, some pits remained and could possibly develop deeper in service conditions. Re-cladding requires removal of the valves, which are welded to the submarine hull, and therefore is very costly. There is then a need to develop techniques to repair these valves in-situ without removing them from the hull.
This project was an exploration of the feasibility of repairing Monel-clad Q1N steel valves, in-situ, using electroless nickel (EN) plating. In this technique, a layer of EN is deposited chemically on the damaged surface. The resistance of the EN coating to both uniform and localized corrosion was compared with that of Monel using electrochemical techniques (i.e. electrochemical impedance spectroscopy and cyclic polarization), and passive crevice corrosion test.

Results
A cleaning technique was developed to allow EN to coat over the bottom of corrosion pits on Monel. The uniform corrosion rate of an EN coating in artificial seawater was found to be less than that of Monel. The tendency towards pitting and crevice corrosion of an EN coating was also found to be better than that of Monel.

Significance
The main conclusion drawn from the current work is that an EN coating would be a viable solution to repair Monel-clad submarine valves.

Future Plans
It is recommended to perform the following tasks in the next phase to further develop this technique to repair Monel-clad Q1N steel valves in situ:

1. Long-term comparison between Monel and EN coating in flowing and stagnant seawater. Measurements include potential, periodic EIS, and metallographic cross-section at the end of the test.
2. Development of the techniques to control the bath ingredients and to deal with the hydrogen evolved during the plating.
3. Determination of the acceptable limits for bath pH, temperature, and concentration of hypophosphite and nickel sulfate.
4. Galvanic corrosion experiment between EN coating and Monel

Prepared by: Y. Wang, DRDC Atlantic/Emat

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Sommaire

Introduction
L'inspection récente des vannes de coque du NCSM VICTORIA a révélé que les vannes de coque en acier Q1N revêtues de Monel étaient endommagées, les dommages les plus graves se présentant sous forme de fissures et de piqûres. La plupart des dommages peuvent être réparés en meulant légèrement le matériau de revêtement, mais certaines piqûres ne peuvent être éliminées, et dans des conditions de service elles pourraient devenir plus profondes. L'application d'un nouveau revêtement implique que les vannes doivent être retirées de leur support et comme elles sont soudées à la coque du sous-marin, la mesure est très coûteuse. Il faut donc mettre au point une technique qui permet de réparer ces vannes in situ, sans les enlever de la coque.
Le présent projet avait pour but d'étudier la faisabilité d'effectuer des réparations in situ de vannes de coque en acier Q1N revêtues de Monel, par dépôt autocatalytique (DA) de nickel. La technique consiste à effectuer le dépôt chimique d'une couche de nickel par DA sur la surface endommagée. On a comparé la résistance à la corrosion uniforme et à la corrosion locale (par piqûres) du revêtement de nickel obtenu par DA et celle du revêtement Monel, à l'aide de techniques électrochimiques (soit la spectroscopie d'impédance électrochimique et la polarisation cyclique) et d'essais de corrosion fissurante passive.

Résultats
On a mis au point une technique de nettoyage permettant d'effectuer le DA de nickel au fond de piqûres de corrosion présentes à la surface du revêtement de Monel. On a mesuré la vitesse de corrosion uniforme d'un revêtement de nickel par DA dans l'eau de mer artificielle; les résultats indiquent que la vitesse de corrosion du revêtement étudié est inférieure à celle du Monel. De plus, le revêtement de nickel par DA résiste mieux que le Monel à la corrosion locale (par piqûres) et à la corrosion fissurante.

Importance des résultats
Les principaux résultats de nos travaux indiquent que le revêtement de nickel par DA constitue une solution de remplacement éprouvée, lorsqu'il faut réparer des vannes de coque de sous-marins revêtues de Monel.

Futurs travaux
Nous recommandons d'exécuter, au cours de la prochaine phase du projet, des travaux additionnels visant à améliorer la technique, afin de pouvoir effectuer la réparation in situ de vannes de coque en acier Q1N revêtues de Monel. En voici la liste :

1. Comparaison à long terme du comportement du revêtement de Monel et du revêtement de nickel par DA, dans l'eau de mer mouvante et stagnante. Les mesures périodiques comprennent celle du potentiel et l'analyse par spectroscopie d'impédance électrochimique [EIS]; l'examen métallographique de coupes transversales sera effectué à la fin de la période d'essai.

2. Mise au point de techniques de régulation de la composition du bain de plaquage et de la production d'hydrogène au cours du traitement.
3. Détermination des valeurs limites acceptables, dans le cas du pH et de la température du bain de plaquage, ainsi que dans celui des concentrations d'hypophosphite et de sulfate de nickel.
4. Exécution d'essais de corrosion galvanique, en présence du revêtement de nickel par DA et du revêtement de Monel.

Préparé par : Y. Wang, RDDC Atlantique/Emat

Roberge, P. R. et Klassen, R. D. 2004. Évaluation de la technique de revêtement autocatalytique pour la réparation in situ de vannes de coque en acier Q1N revêtues de Monel de sous-marins de la classe VICTORIA. RDDC Atlantique CR 2004-226, R & D pour la défense Canada – Atlantique.

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Acknowledgements

The BET surface area of the EN foils was done by Dr. Mike Evans and Dr. Sepp Liang of the Royal Military College of Canada.

1. Introduction

Recent inspection of the hull valves in HMCS VICTORIA revealed damage on the Monel-clad Q1N steel valves. Some damage was in the form of grooves or pits as shown in Figure 1. Other damage was in the form of shallow connected pits as shown in Figure 2. Although most damage can be removed by slightly grinding the cladding material, some pits remained and could possibly develop deeper under certain service conditions. Re-cladding requires removal of the valves, which are welded to the submarine hull, and therefore is very costly. There is then a need to develop techniques to repair these valves in-situ without disconnecting them from the hull.

UNS NO4400 (Monel 400) is an alloy consisting primarily of nickel and copper. The specified composition is 31.5% copper, 1.2 % iron, 1.1% manganese with the balance being nickel. Cladded UNS NO4400 contains higher levels of iron due to mixing with the underlying steel during welding.

The corrosion behavior of UNS NO4400 (Monel 400) in seawater has been studied off and on for over fifty years. The corrosion rate of Monel in strongly agitated and aerated seawater was listed as 5 to 61 μm/y (p. 408) as compared to 50 μm/y (p. 64) for copper[1]. Exposure to stagnant seawater causes marine organisms to accumulate and induce local oxygen concentration cell action followed by pitting.

In the 1940's, the corrosion rate of a range of copper/nickel materials in seawater was measured with particular interest in the mode of corrosion, i.e. uniform or localized[2]. Figure 3 summarizes these results. With materials with a nickel content less than about 50%, there are little or no biofouling and corrosion proceeds uniformly. Above a nickel content of 50%, which includes Monel, the metal permits biofouling and corrodes primarily by pitting.

The corrosion rate of Monel is a function of fluid velocity lists the corrosion rate as <4 μm/y for fluid flow < 1.2 m/s and 16 μm/y for fluid flow at 8.2 m/s (p. 923)[3]. The lower corrosion rates than those reported by Refs. 1 and 2 may reflect better control of impurities during manufacturing.

Welded plates of UNS NO4400 were exposed to artificial seawater containing sulfate-reducing bacteria (SRB) in alternating cycles of aerobic/anaerobic conditions for five months[4]. Localized corrosion in the form of pitting, intergranular corrosion and dealloying was observed.

Both laboratory and field immersion tests on Monel 400 were done to assess its susceptibility towards microbial attack in Arabian Gulf seawater[5]. Specimens were exposed to chlorinated and non-chlorinated seawater for up to four months. The

results indicated that SRB attack was initiated beneath a black sulfide-rich deposit, overlaid by a green chloride-rich deposit, which in turn, was occasionally overlaid by a beige scale on top. The black layer was comprised of iron nickel sulfides, the green layer was essentially $CuCl_2.3Cu(OH)_2/NiCl_2$ and the beige layer was a calcareous deposit.

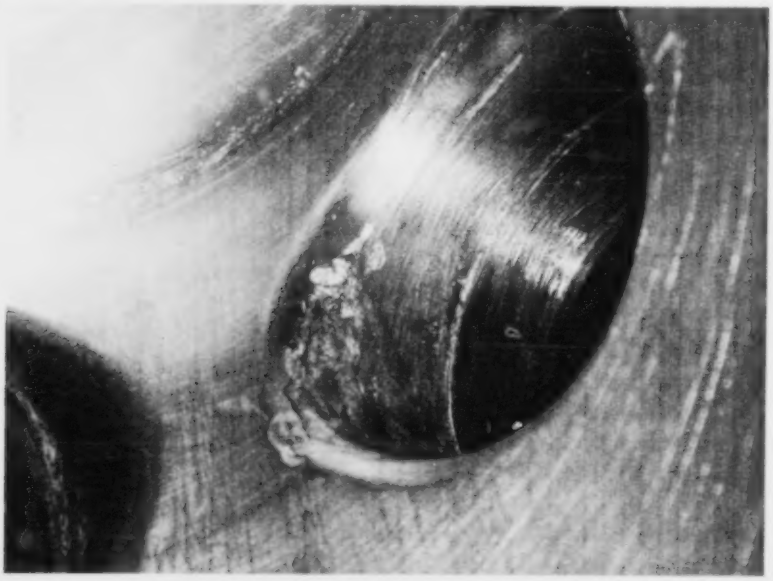

Figure 1. **Photo of DSW 444 valve showing corrosion damage by grooves or pits.**

Selective dealloying of nickel was observed at the bottom of pits of Monel 400 in the presence of SRB[6]. Confocal laser scanning microscopy and scanning vibrating electrode microscopy were used to demonstrate that marine bacteria and anodic sites were co-located.

Studies on the heat-affected zones of copper-nickel piping[7] revealed that welds provide unique environments for the colonization of SRB. Selective sulfide reactions occur within the weld and heat-affected zones of Cu/Ni weldments, thus resulting in selective attack.

The valves are made of steel clad by welding strips of Monel. As mentioned, this process incorporates iron into Monel. Iron levels up to 15% did not increase the tendency of UNS NO4400 to suffer crevice corrosion[8].

Since the Monel-clad Q1N valves are welded to the hull, repair by electroplating is not an option. Therefore, applying a coating of nickel by electroless nickel plating seems to be the only potential approach for repair.

Figure 2. **Photo of SW228 valve showing shallow connecting pits.**

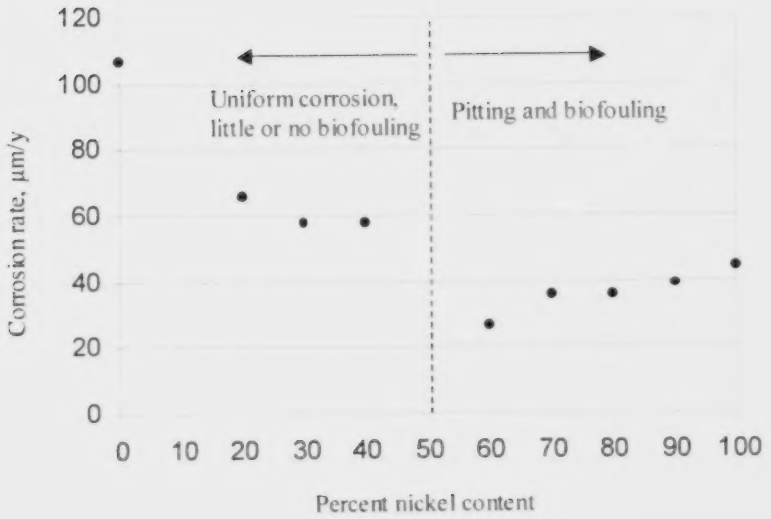

Figure 3. Corrosion rate of copper/nickel materials in seawater with observations on the presence or absence of biofouling and the mode of corrosion.

2. Background on Electroless Nickel Coatings

An extensive compilation of observations about electroless nickel (EN) coatings is Ref. 9. The corrosion rate of an EN coating at room temperature was listed as <2.5 μm/y (p. 141). In CO_2-saturated seawater, the penetration rates ranged from 4 to 22 μm/y (p. 133). In general, EN coatings with fewer impurities and more phosphorous (> 10.5%) performed best. These rates are slightly lower than those reported for Monel. However, since conditions may not have been identical, these results must be considered with cautious optimism.

The EN coating process is purely chemical. A metal is deposited from solution by a reduction reaction. Most commercial processes employ hypophosphite under acidic conditions for the complementary oxidation reaction. The overall reaction may be broadly written as

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni^0 \quad (1)$$

Dissolved nickel (sulfate) is reduced to metallic nickel. Sodium hypophosphite is oxidized to sodium dihydrogenphosphate (III). Both hydrogen gas and sulfuric acid are bi-products. The oxidation of hypophosphite requires energy and a catalyst. Energy is provided from the thermal energy of the bath, which is usually held between 85° and 95°C. The requirement of a catalytic surface impacts the type of metal that can be coated and the surface preparation.

Nickel is catalytic to hypophosphite oxidation whereas copper is not. A vendor (EN-Plate) with experience in coating UNS NO4400 with electroless nickel activated it with an electrodeposition of nickel. This involves passing current through the work piece (cathodically) in a solution of nickel chloride and hydrochloric acid. The idea is to electrolytically deposit a thin layer of nickel, which can then act as a catalyst for EN deposition. Since electrolysis is impossible because the valves to be repaired are electrically connected to the submarine hull, the development of an alternate surface preparation procedure was necessary as described in Section 4.1.

Once started, the main factors that influence the rate of deposition and phosphorous content of an EN coating are bath temperature, pH and bath composition. Increasing bath temperature increases the deposition rate and decreases the phosphorous content of the coating. Similarly, increasing the pH from 4 to 6 increases the deposition rate and decreases the phosphorous content. In general, deposition rate is only slightly affected by nickel concentration in solution. Typically, nickel concentration lies in the range 4 to 8 g/l. However, the ratio of reducing agent (hypophosphite) to nickel has a marked effect. The optimum molar ratio of nickel to hypophosphite should be maintained between 0.3 and 0.45.

Maintaining a bath within operating limits becomes a challenge during deposition. This is because sulfuric acid is produced, which lowers the pH, and the reducing agent is consumed at a rate of three moles per mole of nickel reduced. The pH may be monitored with an electronic pH meter or pH papers. The concentration of nickel may be obtained by titrating a sample with EDTA (ethylenediamine tetra-acetic acid). Similarly, the concentration of reducing agent and spent reducing agent may be obtained by a suitable titration. Determination of the concentration of organic acids and stabilizer is best carried out using liquid chromatography.

EN coatings are not pore-free. Ref. 9 shows SEM micrographs that indicate one class of pores at 5000X magnification and another class at 20,000X magnification. Porosity is a result of escaping hydrogen gas, a product of the reaction shown in Eq. (1). Porosity and, possibly, the inclusion of phosphorous, decreases coating density somewhat. The density of pure nickel is 8.9 g/cm^3 and that for EN coatings is typically between 7.9 and 8.2 g/cm^3.

3. Experimental

The experimental objectives of this project were to test the ability of an EN coating to cover a pitted Monel sample and to measure its corrosion resistance under conditions that normally promote Monel to corrode. However, attempts to characterize the pitting behavior of Monel in artificial seawater using electrochemical noise were disappointing because the samples simply did not pit reliably. Even if they did pit reliably in artificial seawater this would not simulate the conditions in natural seawater where Monel pits due to the activity of SRB, which is difficult and time-consuming to simulate in the laboratory (Refs. 4-8). Fortunately, a bar of naturally-corroded Monel was available for experimentation. Therefore, our experimental goals were modified to: (i) identify a cleaning procedure that enables the bottom of pits to be coated with EN without resorting to commercially-standard electrolysis techniques and (ii) measure the corrosion characteristics of EN-coated Monel and Monel in artificial seawater using laboratory techniques.

A sample of naturally-corroded Monel was provided by Dr. Calvin Hyatt from DRDC Atlantic. It was a bar measuring about 30 cm in length, 4 cm in width and 0.7 cm in depth. It had been bolted to a larger plate and then exposed to seawater near the Halifax harbor. The exposed sides were either black or covered with pits that were filled with green material. Plates of uncorroded Monel 400 were available as well as finger ingots of mixtures of Monel 400 and HY 80 steel from a previous contract[8]. Samples of uncorroded Monel for electrochemical characterization were made by encasing into epoxy moulds after soldering a wire to each. The exposed surface area was approximately 1 cm^2. Some of these Monel samples were coated with EN. The artificial seawater was made according to ASTM D 1141[10].

The EN coating process was carried out by heating 2 liters of bath liquid in a glass vessel with a hot-plate/stirrer. A thermometer indicated the bath temperature. The bath temperature was manually controlled by the rate of heat input through the hot plate. The composition of the EN bath used was formulation No. 1 (Table 2) in ASTM B 656[11]. The pH was adjusted to between 4.5 and 5.0 as per this formula with pellets of sodium hydroxide. The bath was operated in batch mode with no attempt to replenish spent reactants or adjust the pH. Typically after an overnight experiment, the pH had dropped to about 3.6.

As a measure of coating porosity, the BET (Brunauer, Emmet, Teller) surface area of a sample of EN coatings was done by Drs. S. Liang and M. Evans with a unit made by Micromeritics (model ASAP 2000). The EN coatings sample was obtained by coating onto the inside wall of the glass vessel. These deposits were readily removed as thin foils.

Both Monel and EN samples were characterized with electrochemical impedance spectroscopy (EIS). The electrolyte was artificial seawater. The frequency range of data collection was from 0.002 to 5,000 Hz. Since each scan took about 1.2 hours the sample had to be reasonably stable. Initial work indicated that Monel was fairly stable after two days. Therefore, a scan was taken after two days of immersion for each sample.

The Monel and EN samples were also characterized with cyclic polarization according the ASTM G 61[12]. Cyclic polarization is intended to provide a semi-quantitative measure of nickel-based alloys to localized corrosion, both pitting and crevice corrosion. A "knee" in the upward polarization curve and hysteresis indicate a tendency towards localized corrosion. A "knee" is where the slope of potential versus current suddenly decreases. The potential where this occurs (for a susceptible material) is called E_{bd}, the breakdown potential. The more electronegative this potential is, the more susceptible the material is to localized corrosion. The larger the hysteresis, the greater the tendency the material has to propagate localized corrosion.

The scanning electron microscope (SEM) used was a Philips XL 30 that was equipped with an EDAX (CPU Leap Detector) for elemental analysis.

The tendency of both Monel and an EN coating to undergo crevice corrosion was tested using ASTM G 78[13]. This test is passive and designed for iron- and nickel-based stainless alloys in chloride-containing environments. It involves covering a metal sample with a plastic washer under a load, i.e. 25 in-lb_f torque. The outer rim of the plastic was segmented into twelve triangular wedges with each wedge providing a crevice. A bolt through the center held the crevice former in place. A crevice former was placed on both sides of a Monel and an EN coated sample. The solution was artificial seawater that was left open to ambient air in our laboratory. Evaporative losses were replaced with deionized water.

4. Results and Discussion

4.1 Characterization of Corroded Monel Sample

Figure 4 is a scanning electron micrograph (SEM) of the bar of Monel exposed in seawater. The smoother region was black and the rougher region was light green. The light green material covered pits. An EDX analysis of these regions is shown in Table 1.

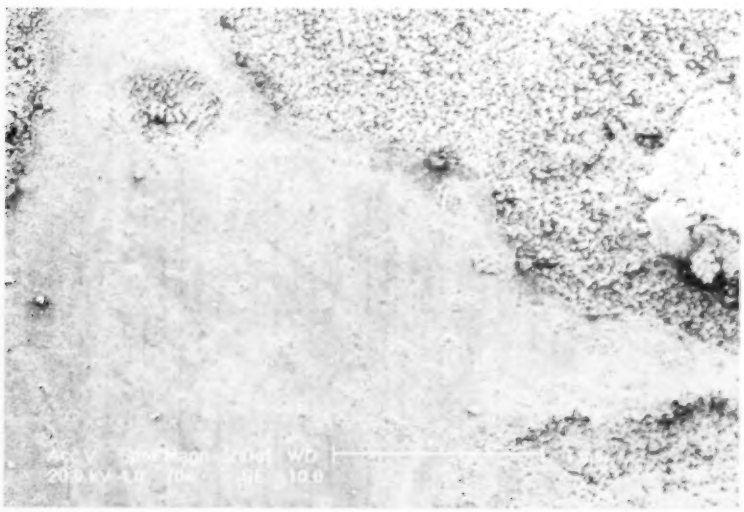

Figure 4. SEM micrograph of corroded Monel bar showing smooth and granular regions, which covered pits.

The more granulated region had a higher level of oxygen indicating more oxide or hydroxide corrosion products. One feature is that the granular region contained titanium. At the time of writing this report the history of the corroded bar was not known and it is possible that there was a galvanic connection to titanium. Another feature was that both regions had corrosion products containing bromide. A typical concentration of bromide in seawater is 0.07 g/kg whereas that for chloride is 19 g/kg. Possibly bromide is more aggressive than chloride in attacking Monel even though it has a much smaller concentration in seawater.

Table 1. Elemental analysis (as weight percent) of granular and smooth regions shown in Fiure 4 of corroded Monel bar.

Element	Smoother region in Figure 4	Granular region in Figure 4
O	11.1	16.0
Br	4.56	9.79
Cl	4.44	7.19
Ti	0.0	3.35
Ni	41.8	34.8
Cu	38.0	28.9

4.2 Surface Preparation

Surface preparation is an issue in this potential application for two reasons. Firstly, the electrical attachment of the valve to the hull precludes the use of two electrolysis preparations that are commercially standard. These include anodic etching in acid and the deposition of a thin-layer of nickel by electrolysis (Wood's nickel strike). Secondly, the grinding process that is allowable may be insufficient to eliminate all traces of pits. Therefore, a means to chemically clean and then activate a pitted Monel surface is necessary.

Samples of the corroded Monel bar described in Section 4.1 were used to test cleaning procedures. A twelve-hour soak in 15% HCl removed most of the blackish tint on the smooth regions and the green deposit in the pits. However, it left black granular crystals at the bottom of the pits. This could be iron-nickel sulfides as described by Ref. 5. A thirty-minute soak in 100% HCl cleaned both the surface and the bottom of pits to a lighter shade. A sample so prepared was active in an EN bath as evidenced by the generation of bubbles (hydrogen) on the surface. After sixteen hours in the batch EN bath, the sample was mounted, cross-sectioned and then polished according to standard metallurgical techniques. The cross-section was then etched for 30s with a solution of 8g $FeCl_3$, 25 ml HCl and 100 ml water (microetchant #38, Ref. 14).

Figure 5 shows a metallurgical micrograph of the Monel sample near a corner. The effect of etchant on Monel was to reveal grains whereas it had no effect on the EN coating. This is because it is amorphous. The depth of EN coating was 170 μm. On smooth sections as this, the EN coating was even. Of interest, however, was how it would follow the contours of a pitted area.

Figure 6 is a metallurgical micrograph of the Monel sample near a pitted area. The EN coating follows the gross profile of the pit. However, on the scale of grains, the EN coating fills in holes. The bottom of pits usually had regions of deeper but narrower excavations.

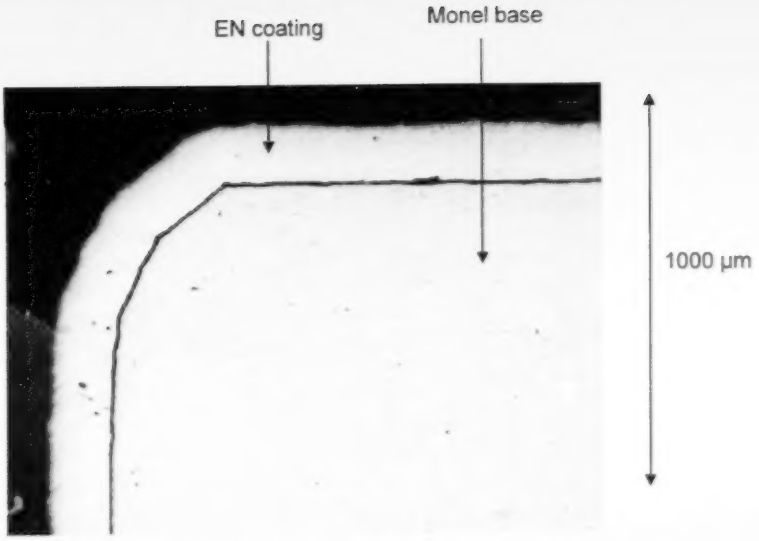

Figure 5. Metallurgical micrograph of a cross-section of a corner of EN-coated Monel sample. The depth of the EN coating was 170 µm.

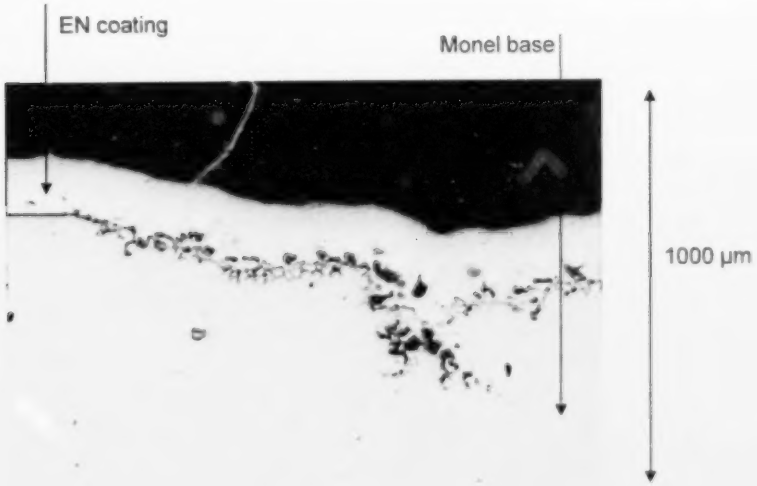

Figure 6. Metallurgical micrograph of a cross-section of a pitted area of EN-coated Monel sample. The depth of the EN coating was 170 µm.

Figure 7 is a metallurgical micrograph near the excavated area at the bottom of a pit. The excavated area appears to be due to the removal of whole grains of Monel as per intergranular corrosion.

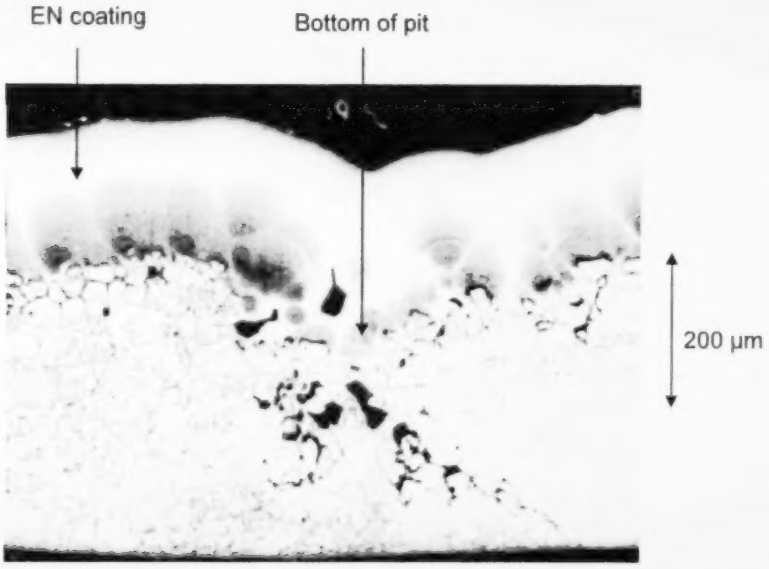

Figure 7. Metallurgical micrograph of a cross-section of excavations within a pitted area of EN-coated Monel sample after etching. The depth of the EN coating was 170 µm.

Therefore, one of the experimental objectives of this project was met. Naturally-corroded Monel can be sufficiently cleaned for EN coating by soaking in 100% hydrochloric acid for thirty minutes. A milder treatment may be possible but this requires experimental verification.

4.3 Characterization of an EN coating

A series of SEM micrographs of an EN coating are shown at increasing magnification in Figures 8, 9 and 10. The appearance is very similar to those shown in Ref. 9. The general topography is like a layer of molten pebbles of various sizes. Pores are evident as black spots that become more prominent as the magnification increases. A typical EDX analysis was 88.3% nickel and 11.7% phosphorous, with a notable lack of oxygen.

Figure 8. SEM micrograph of an electroless nickel coating on Monel (2000X).

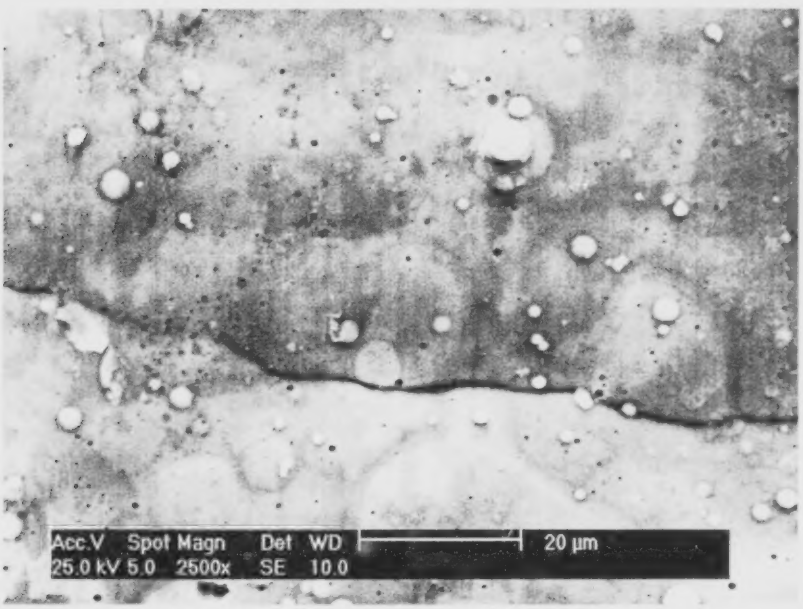

Figure 9. SEM micrograph of an electroless nickel coating on Monel (2500X).

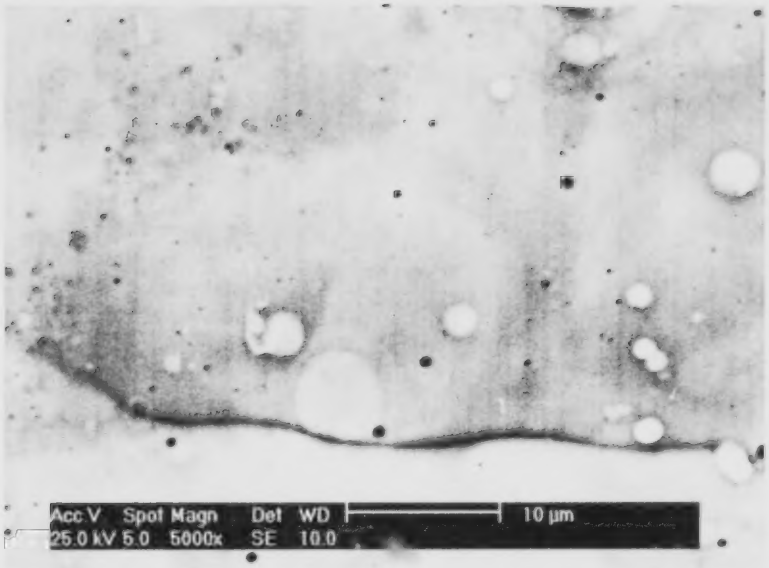

Figure 10. SEM micrograph of an electroless nickel coating on Monel (5000X).

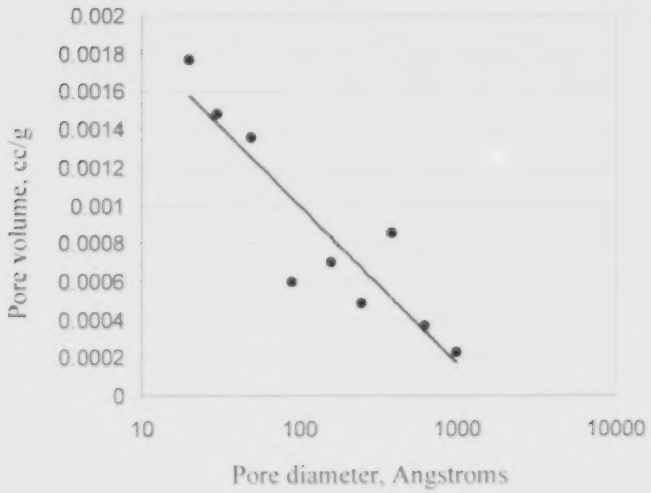

Figure 11. **Pore volume versus pore diameter for the EN foils as measured by BET surface area measurement**

The BET surface area was obtained for EN foils that deposited onto the inside surface of the glass container. The BET surface area of these foils was 2.51 ± 0.86 m^2/g based on multi-point analysis. The pore volume versus pore diameter is shown in Figure 10.

The largest pin-hole defect seen in the SEM micrographs was about 1 μm, which corresponds to 10,000 Angstroms. From the measurements shown in Figure 11, most of the pore volume and therefore surface area are in pores smaller than 0.1 μm. Thus the SEM micrographs suggest that the BET surface area measurement was plausible.

4.4 Electrochemical Impedance Spectroscopy

The EIS measurement of a Monel sample in seawater is shown in Figure 12 and that for an EN coated Monel sample in seawater is shown in Figure 13. The Nyquist representation of these data is shown in Figures 14 and 15. Two humps are clearly seen with the Monel sample and are subtly evident with the EN-coated sample. Thus the analogue electrical circuit required to fit this data requires two RC subcircuits, which is typical of a surface with an anodic film[16]. The lack of a mass-transfer resistance (i.e. a Warburg) for the EN-coated Monel indicated that electrolyte did not permeate the EN coating and therefore the anodic film was on top of the EN coating. Therefore, the tiny pores evident from both the SEM micrographs and the measurable BET surface area are not interconnected enough to allow penetration of electrolyte to the underlying metal. The electrical analogue circuit used to fit the EIS data for both samples is shown in Figure 16. The R_{soln} accounts for solution resistance between the sample and counter electrode. The R_{film} accounts for the resistance of a film layer. The R_{cor} accounts for the charge transfer resistance at the metal surface, i.e. the polarization resistance. The capacitance at the metal surface and within the film was modeled as constant phase elements. These contain two parameters; a pseudo capacitance and an exponent. An exponent of unity indicates a pure capacitor and less than unity indicates a dispersion of capacitor effects. The fitted parameters to the analogue circuit to the EIS data are shown in Figures 14 and 15 as the "fit" curve and are listed in Table 2.

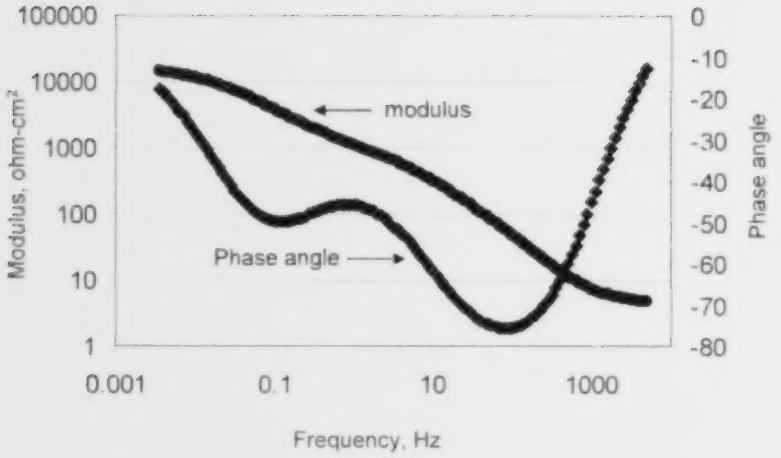

Figure 12. **Bode diagram of the EIS measurements for Monel in artificial seawater.**

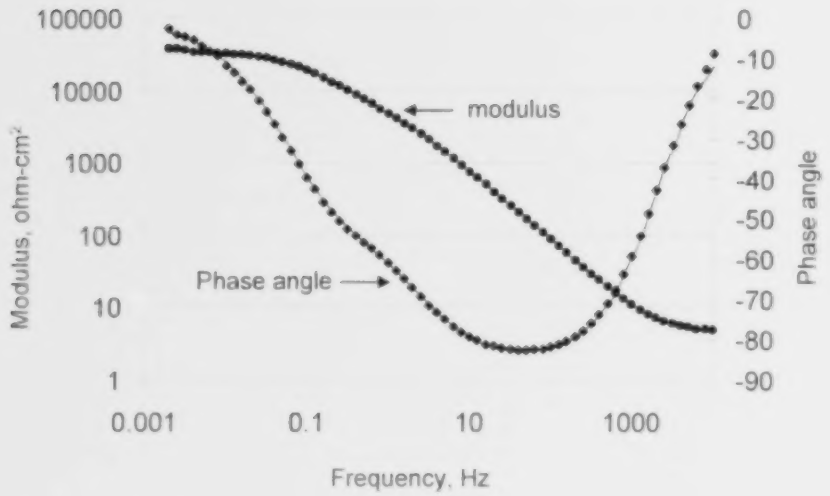

Figure 13. **Bode diagram of the EIS measurements for EN-coated Monel in artificial seawater.**

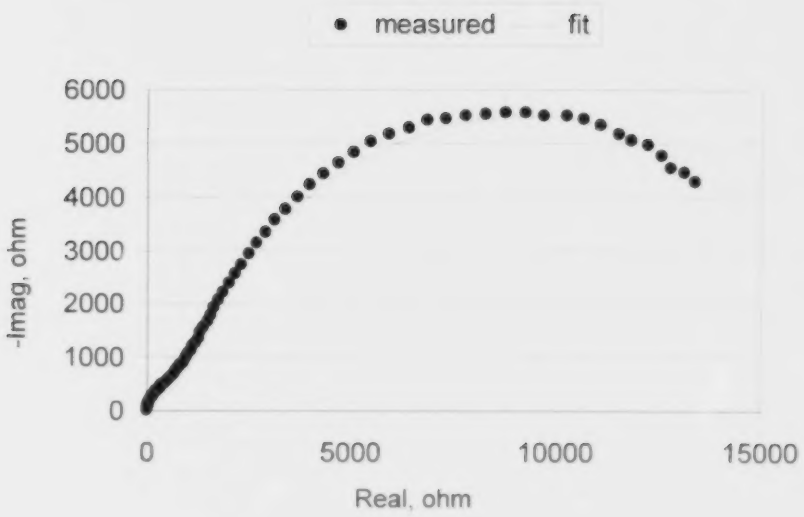

Figure 14. **Nyquist representation of the Monel sample in artificial seawater (Bode representation shown in Figure 12).**

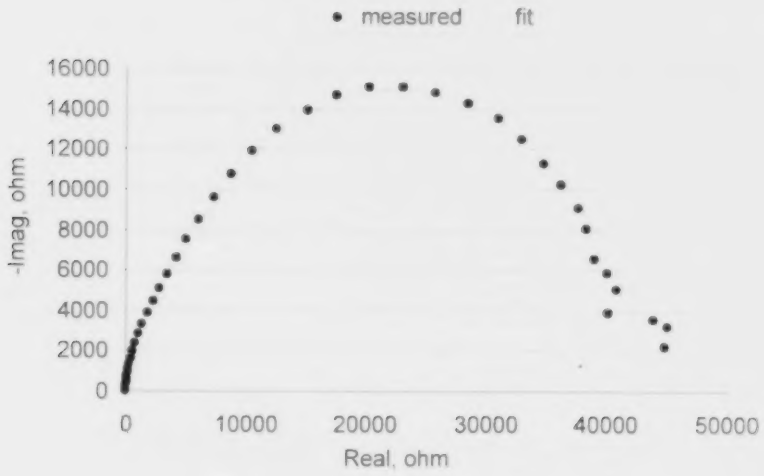

Figure 15. **Nyquist representation of the EN-coated Monel sample in artificial seawater (Bode representation shown in Figure 13).**

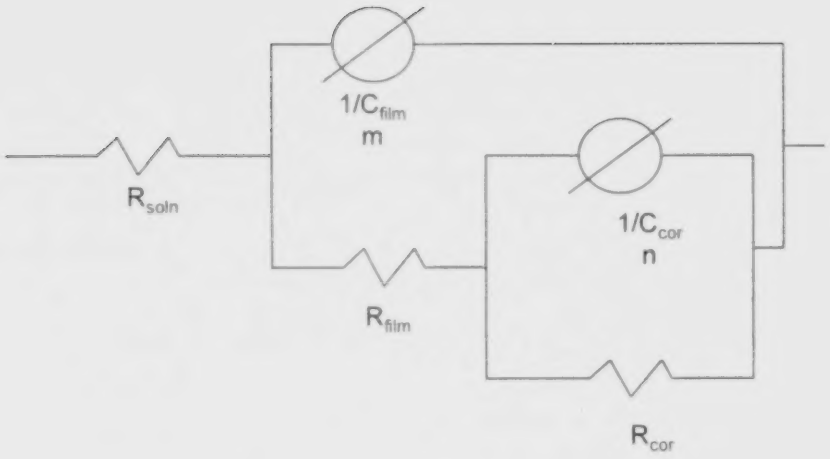

Figure 16. **Schematic of the electrical analogue used for interpreting EIS data shown in Figures 12 and 13.**

Table 2. **Fitted parameters of the EIS data in Figures 12 and 13 to the electrical analogue shown in Figure 16. The R_{cor} was corrected for the actual area of 0.81 cm^2.**

Parameter	Monel (Figure 8)		EN-coated Monel (Figure 9)	
R_{soln}, ohm	4.58	± 0.005	R_{soln}, ohm	4.58
R_{cor}, ohm-cm^2	17340	± 342	R_{cor}, ohm-cm^2	17340
$1/C_{cor}$	3115	± 32	$1/C_{cor}$	3115
n	0.70	± 0.007	n	0.70
R_{film}, ohm-cm^2	800	± 24	R_{film}, ohm-cm^2	800
$1/C_{film}$	18430	± 432	$1/C_{film}$	18430
m	0.93	± 0.003	m	0.93

The polarization resistance, as interpreted as R_{cor}, is higher for the EN coating than that for Monel. This indicates that an EN coating will tend to corrode at a slower rate than Monel in seawater. Both Monel and EN coating form an oxide layer from initial corrosion products that is protective against further corrosion. The film resistance for the EN coating is much higher than that for the native oxide (6094 ohms versus 800 ohms), possibly indicating a thicker or less conductive film.

The polarization resistance measured by EIS is a measure of the uniform corrosion rate as opposed to tendency towards localized corrosion. The latter was measured by cyclic polarization as per ASTM G 61.

4.5 Cyclic Polarization

Cyclic polarization curves for Monel 400 and an EN coating are shown in Figure 17. The "knee" in the potential/current plot for the Monel 400 clearly shows a tendency towards localized corrosion in seawater. This is no surprise since the valves in Figures 1 and 2 indicate localized corrosion after service in seawater. The EN coating does not seem to exhibit a tendency towards localized corrosion. If substantiated by another test then this characteristic is an important advantage to an EN coating.

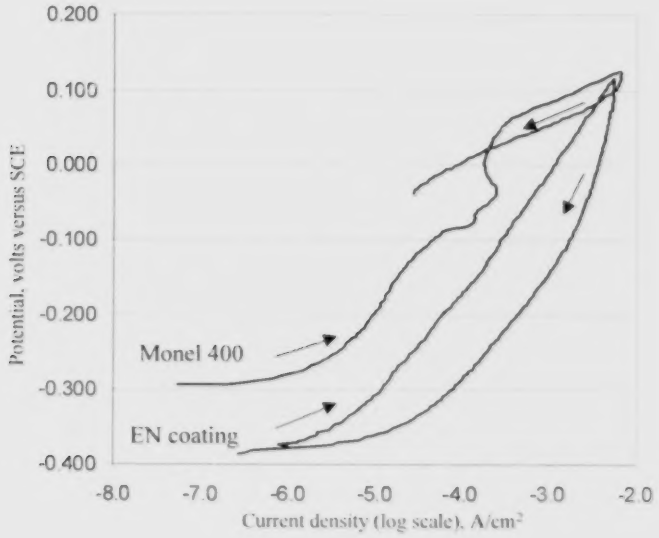

Figure 17. Cyclic polarization results for Monel and EN coating.

4.6 Passive Crevice Test

After nine weeks, the crevice formers were removed. The outline of each crevice wedge was faintly visible on both the Monel and EN samples. SEM micrographs were taken of the wedge area for each sample. Figure 18 shows the wedge area for Monel and Figure 19 shows a wedge area for the EN coating. The build-up of corrosion products around the wedge perimeter is thicker for Monel than the EN coating. This indicates that Monel corroded more underneath the wedge crevice than the EN sample.

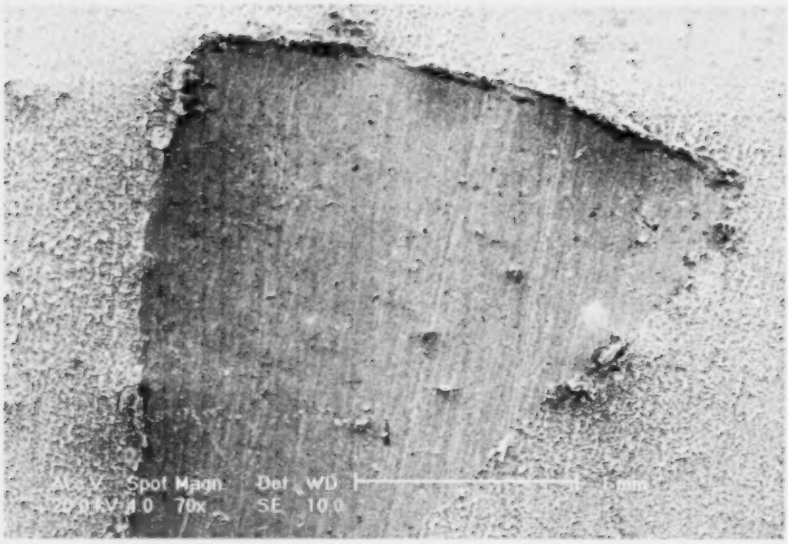

Figure 18. SEM micrograph of the crevice wedge area for Monel (after nine weeks exposure to artificial seawater).

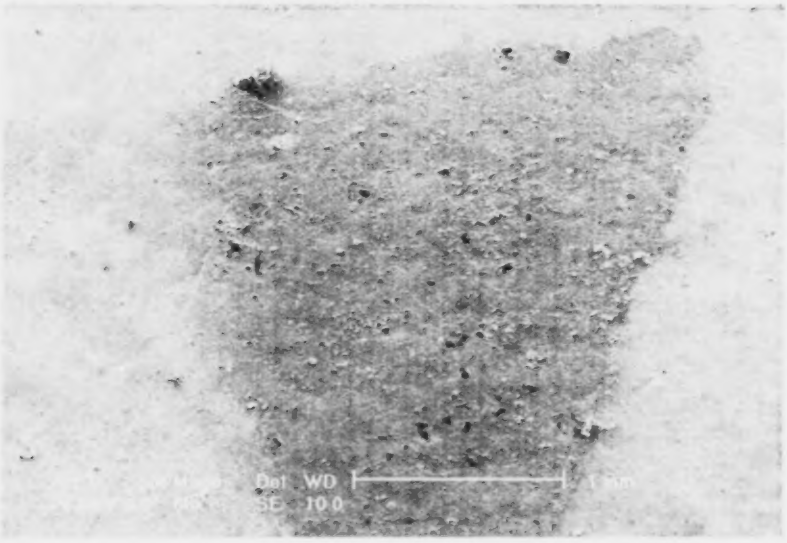

Figure 19. SEM micrograph of the crevice wedge area for EN-coated Monel (after nine weeks exposure to artificial seawater).

5. Preliminary Design for Coating Submarine Valves

A system for metallizing submarine hull valves with electroless nickel needs to account for the following constraints:

i. The valve body is welded to the hull.
ii. The valve interior is accessible by flanged connections.
iii. The operating temperature of the EN bath is 85-95°C.
iv. Hydrogen gas is a product of the coating process.
v. Hydrochloric acid (probably 100% strength) is necessary to clean valve internals prior to coating.
vi. The valve interior is too small to contain enough EN bath to coat valve internals.
vii. The EN bath liquid changes composition as coating proceeds and reactants must be re-supplied and the pH adjusted.

A schematic of such a system is shown in Figure 20.

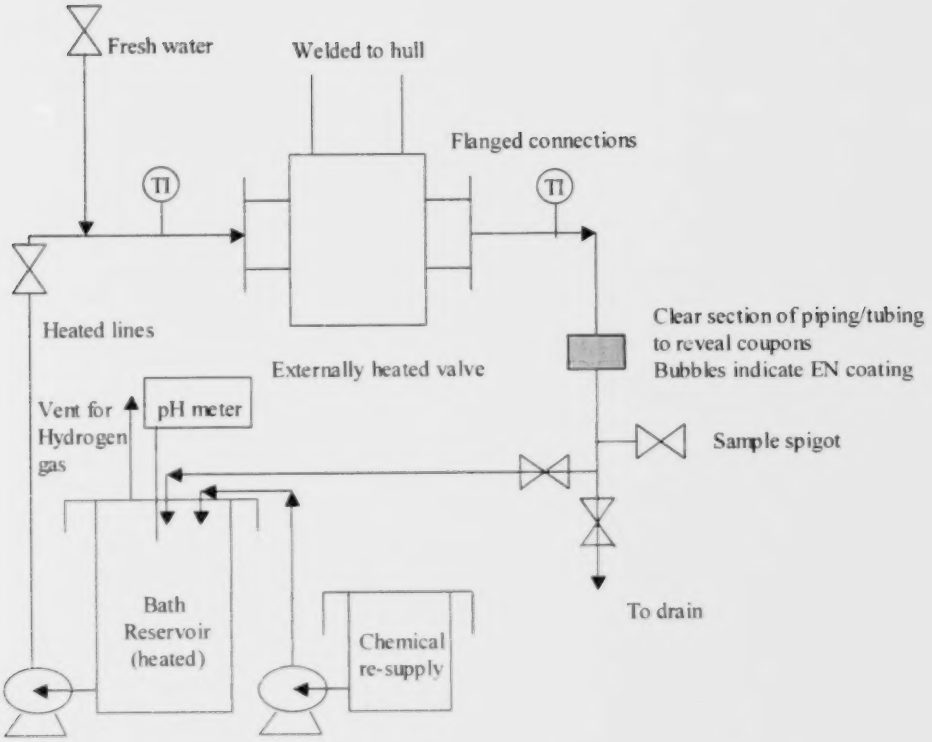

Figure 20. Schematic of a preliminary design for coating submarine hull valves.

6. Conclusions

This project was an exploration of the feasibility of repairing submarine hull valves, in-situ, using electroless nickel. The main conclusion is that this approach appears to be feasible for the following reasons:

i. Cleaning corroded Monel with hydrochloric acid (100% for 30 minutes) is sufficient to allow EN to coat over the bottom of pits. Thus, cleaning steps used in commercial operations that involve electrolysis, such as anodic etching and the Wood's nickel strike, are not necessary.
ii. The uniform corrosion rate of an EN coating in artificial seawater, as measured by electrochemical impedance spectroscopy, is less than that for Monel. This is consistent with literature data for both.
iii. The tendency towards pitting and crevice corrosion of an EN coating is no more than that for Monel and likely less so.

It is recommended that detailed engineering and supportive laboratory work be done to develop this technique to repair Monel valves in situ.

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This project was an exploration of the feasibility of repairing Monel-clad Q1N steel valves, in-situ, using electroless nickel (EN) plating. In this technique, a layer of EN is deposited chemically on the damaged surface. The resistance of the EN coating to both uniform and localized corrosion was compared with that of Monel using electrochemical techniques (i.e. electrochemical impedance spectroscopy and cyclic polarization), and passive crevice corrosion test.

A cleaning technique was developed to allow EN to coat over the bottom of corrosion pits on Monel. The uniform corrosion rate of an EN coating in artificial seawater was measured by electrochemical impedance spectroscopy and found to be less than that of Monel. The tendency towards pitting and crevice corrosion of an EN coating was also found to be better than that of Monel. The main conclusion from this work is that an EN coating would be a viable solution to repair Monel-clad submarine valves. Recommendations were also made to further develop the EN technique to repair Monel-clad Q1N steel valves in situ.

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